

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 20 February 2001 (20.02.01)	
International application No. PCT/GB00/02255	Applicant's or agent's file reference MJ/CS/STS.38
International filing date (day/month/year) 21 June 2000 (21.06.00)	Priority date (day/month/year) 21 June 1999 (21.06.99)
Applicant ANAND, Srinivasan et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

15 January 2001 (15.01.01)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Juan Cruz Telephone No.: (41-22) 338.83.38
---	---

P. ENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

JAMES, Michael, John, Gwynne
Wynne-Jones Laine & James
22 Rodney Road
Cheltenham
Gloucestershire GL50 1JJ
ROYAUME-UNI

Date of mailing (day/month/year) 01 February 2001 (01.02.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference MJ/CS/STS.38	
International application No. PCT/GB00/02255	International filing date (day/month/year) 21 June 2000 (21.06.00)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input checked="" type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address SRINIVASAN, Anand Kavlevagen 151 S-141 59 Huddinge Sweden	State of Nationality IN	State of Residence SE
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input type="checkbox"/> the person	<input checked="" type="checkbox"/> the name	<input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address ANAND, Srinivasan Kavlevagen 151 S-141 59 Huddinge Sweden	State of Nationality IN	State of Residence SE
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary:		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input checked="" type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input type="checkbox"/> the elected Offices concerned	
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Christine Carrié
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference MJ/CS/STS.38	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 00/ 02255	International filing date (day/month/year) 21/06/2000	(Earliest) Priority Date (day/month/year) 21/06/1999
Applicant SURFACE TECHNOLOGY SYSTEMS LIMITED		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of Invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/306 H01L21/465

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 534 109 A (FUJIWARA KOJI ET AL) 9 July 1996 (1996-07-09) claim 3	1-12
P, X	C.F. CARLSTRÖM, S. ANAND, G. LANDGREN: "Trimethylamine : Novel source for low damage reactive ion beam etching of InP" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY B, vol. 17, no. 6, November 1999 (1999-11), pages 2660-2663, XP002150318 the whole document --- -/--	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

17 October 2000

Date of mailing of the international search report

06/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Le Meur, M-A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 016896 A (FUJITSU LTD), 22 January 1999 (1999-01-22) abstract -----	1
A	US 5 527 425 A (HOBSON WILLIAM S ET AL) 18 June 1996 (1996-06-18) the whole document -----	4-12
A	ELKIND J L ET AL: "REACTIVE ION ETCHING OF HGCDTE WITH METHANE AND HYDROGEN" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, US, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 10, no. 4 PT I, 1 July 1992 (1992-07-01), pages 1106-1112, XP000296215 ISSN: 0734-2101 page 1106, left-hand column, line 12 - line 14 -----	10, 11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/02255

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5534109	A	09-07-1996	JP 7201820 A		04-08-1995
			FR 2714526 A		30-06-1995
JP 11016896	A	22-01-1999	NONE		
US 5527425	A	18-06-1996	EP 0755069 A		22-01-1997
			JP 9036104 A		07-02-1997

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 December 2000 (28.12.2000)

PCT

(10) International Publication Number
WO 00/79578 A1

(51) International Patent Classification⁷: **H01L 21/306,**
21/465

(SE). CARLSTROM, Carl-Fredrik [SE/SE]; Filipstads-
backen 56, S-123 43 Farsta (SE). LANDGREN, Gunnar
[SE/SE]; Landsvagen 31, S-192 70 Sollentuna (SE).

(21) International Application Number: PCT/GB00/02255

(22) International Filing Date: 21 June 2000 (21.06.2000)

(74) Agents: JAMES, Michael, John, Gwynne et al.;
Wynne-Jones Laine & James, 22 Rodney Road, Chel-
tenham, Gloucestershire GL50 1JJ (GB).

(25) Filing Language: English

(81) Designated States (*national*): JP, KR, US.

(26) Publication Language: English

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE).

(30) Priority Data:
9902344-2 21 June 1999 (21.06.1999) SE
9903213-8 10 September 1999 (10.09.1999) SE

Published:

- With international search report.
- Before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments.

(71) Applicant (*for all designated States except US*):
SURFACE TECHNOLOGY SYSTEMS LIMITED
[GB/GB]; Imperial Park, Newport, Gwent NP1 9UJ (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): SRINIVASAN,
Anand [IN/SE]; Kavlevagen 151, S-141 59 Huddinge

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*



WO 00/79578 A1

(54) Title: IMPROVEMENTS RELATING TO PLASMA ETCHING

(57) Abstract: A substrate whose elemental constituents are selected from Groups III and V of the Periodic Table, is provided with pre-defined masked regions. Etching of the substrate comprising the steps of: a) forming a gas containing molecules having at least one methyl group (CH₃) linked to nitrogen into a plasma; and b) etching the unmasked regions of the substrate by means of the plasma. For a substrate whose elemental constituents are selected from Groups II and VI of the Periodic Table, the plasma etching gas used is trimethylamine. Since the methyl compound of nitrogen has a lower bond energy than for hydrocarbon mixtures, free methyl radicals are easier to obtain and the gas is more efficient as a methyl source. In addition, compared with hydrocarbon mixtures, reduced polymer formation can be expected due to preferential formation of methyl radicals over polymer-generating hydrocarbon radicals because of the lower bond energy for the former.

"Improvements relating to plasma etching"

The present invention relates to a method of etching and finds particular application in the fields of opto-electronic, electronic and micro-mechanical device production.

Many semiconductor devices consist of at least one element selected of Group III and at least one element selected of Group V of the periodic table (III-V materials). Examples of such materials include indium phosphide (InP), gallium arsenide (GaAs), the ternary ($\text{In}_x\text{Ga}_{1-x}\text{As}$) and the quaternary materials ($\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$).

The production of semiconductor devices generally involves the processing of the surface of a solid substrate, either by etching or by deposition. A known method of processing a solid substrate is to expose the substrate to a plasma of a gas having the glow discharges of the gas molecules reacting chemically and/or physically with the substrate.

III-V materials can be etched using hydrocarbon gases. In the book by Avishay Katz "Indium Phosphide and Related Materials, Processing, Technology and Devices", Artech House Boston, London, methods of etching InP and related materials are described.

It is considered in the above book that etching of the substrate surface is caused by formation of volatile organometal species (i.e. methyl-III compounds e.g. $(\text{CH}_3)_x\text{In}$) and hydrogen-V compounds.

The formation of organometal species, especially $(\text{CH}_3)_x\text{In}$, is crucial since the V-elements, especially phosphorus, are volatile and depletion of the group V-element on the surface can occur. The enrichment of III-elements, especially indium, leads to the micro-masking effect where indium rich areas are more difficult to etch and thereby mask the underlying crystal resulting in rough surface morphology.

However, increase of the hydrocarbon etch gas to compensate with a higher indium methyl formation rate leads to formation of an etch inhibiting polymer film on the surface and severe polymer build-up on the mask.

It is one object of the present invention to provide a method of etching with enhanced etching of the III elements, avoiding preferential etching of the V elements.

According to the present invention, there is provided a method of etching a substrate provided with pre-defined masked regions, whose elemental constituents are selected from Groups III and V of the Periodic Table, which method provides free methyl radicals in a plasma environment using a gas including a methyl compound bonded to nitrogen.

In particular, methylamine (CH_3NH_2), dimethylamine ($(\text{CH}_3)_2\text{NH}$) and trimethylamine ($(\text{CH}_3)_3\text{N}$) can be used as the etch gas. Preferred substrate materials comprise InN, InP, InAs, InSb, InGaAs, InGaAsP, GaN, GaP, GaAs, GaSb, AlP, AlAs, AlSb, AlGaAs, AlGaN and AlGaInN compounds

Further, not only the above-mentioned materials, whose

surface elemental constituents are selected from Groups III and V of the Periodic Table, can be etched, but also materials whose surface elemental constituents are selected from Groups II and VI of the Periodic Table, with said etchant gas, but preferably using trimethylamine as the etchant gas. Preferred such materials comprise CdS, CdSe, CdTe, HgS, HgSe, HgTe, MgS, MgSe, MgTe, MnS, MnSe, MnTe, PbS, PbSe, PbTe, SnS, SnSe, SnTe, ZnS, ZnSe, ZnTe, CdHgTe and other alloys based on these compounds.

It may be preferred that the etch gas comprising a methyl compound bonded to nitrogen should be mixed with another gas. Such additional gas may comprise H_2 , N_2 , O_2 , a rare gas (such as Ar) or a halogen-containing gas (such as Cl_2 , BCl_3) or any combination of these.

It has been found that methods according to the embodiment of the present invention can reduce the disadvantage mentioned above in that a much smoother ion beam etched surface is produced.

Further, low polymer formation is expected due to preferential formation of methyl radicals over polymer-generating hydrocarbon radicals because of the lower bond energy for the former. This allows higher methyl containing gasflows to counter the preferential etching of the V elements, while maintaining a low polymer formation, which increases the parameter space useful for process optimisation.

Furthermore, it is possible to apply plasma etching

other than ion beam etching, in which is used the above-mentioned etching gas that has been formed into a plasma, by supplying microwave electric power with a magnetic field, supplying microwave electric power alone, supplying
5 radio frequency electric power or supplying DC-power. This application leads to enhanced etching of the III element in a III/V compound material to counter preferential removal of the V element.

The invention may be performed in various ways and
10 preferred embodiments thereof will now be described, by way of example, with reference to the accompanying drawings, in which:-

Figure 1 is a side view showing a structure of an inductively coupled plasma ion beam etching apparatus used
15 in an etching method according to an embodiment of the present invention;

Figure 2 is a side view showing a structure of a parallel plate type plasma etching apparatus used in an etching method according to an embodiment of the present
20 invention;

Figure 3 is a side view showing a structure of an electron cyclotron resonance (ECR) etching apparatus used in an etching method according to an embodiment of the present invention;

25 Figure 4 is a side view showing a structure of an inductively coupled plasma (ICP) etching apparatus used in an etching method according to an embodiment of the present

invention;

Figure 5 is a side view showing a structure of a barrel reactor plasma etching apparatus used in an etching method according to an embodiment of the present invention;

5 Figure 6 is a side view showing a structure of an electron cyclotron resonance plasma ion beam etching apparatus used in an etching method according to an embodiment of the present invention;

10 Figure 7A is a cross sectional view showing an InP sample with resist mask;

Figure 7B is a cross sectional view showing an etched InP sample after removal of the resist mark;

15 Figure 8 is scanning electron microscopy picture showing test structures in InP after etching based on an etching method according to an embodiment of the present invention; and

Figure 9 is a side view showing a structure of a diode type plasma etching apparatus used in an etching method according to an embodiment of the present invention.

20 Table 1 shows, by atomic force microscopy, the measured root mean square (rms.) roughness of InP surfaces etched using different energies. The first two columns show rms. roughness of InP surfaces etched by etching methods according to an embodiment of the present
25 invention. The last column shows the rms. roughness of InP surfaces etched by standard Ar sputtering.

A method for etching an InP substrate according to the

embodiment of the present invention will now be described with reference to the drawings.

(1) Description of an inductively coupled radio-frequency plasma (ICP) ion beam etching system used in a method for etching an InP substrate according to an embodiment of the present invention.

In Figure 1, a plasma generating chamber 1 is used for forming plasma. The plasma is generated by inductive coupling of 13.56 MHz RF-power from a coil 6 to the plasma generating chamber 1. The RF-power is coupled from the coil 6 to the plasma generating chamber 1 through a dielectric coupling window 8 which isolates the vacuum in the plasma generating chamber 1 from the atmospheric pressure at the coil 6. An etching chamber 2 is connected to the plasma generating chamber 1 through an extracting grid 3 and an acceleration grid 4. Ions in the plasma generated in the plasma generating chamber 1 are accelerated towards an InP substrate 10 by applying a negative bias on the extraction grid 3 and a positive bias on the acceleration grid 4. The InP substrate 10 is placed on the substrate table 11 which is grounded with respect to the extraction grid 3 and the acceleration grid 4.

Permanent magnets 5 enhance the RF-power coupling from coil 6 to the gas plasma in the plasma generating chamber. The gas is injected to the plasma generating chamber 1 through the gas introduction holes 7. An exhaust port 9 is provided from the etching chamber 2, and excessive etching

gas and reacted gas are exhausted therethrough to the outside of the etching chamber.

This inductively coupled radio frequency plasma ion beam etching system has such features that the energy of the ions impinging on the target can be controlled in the range from a few eV up to 900 eV. Further, there is also the feature that etching can be made without significant heating of the substrate i.e. close to room temperature.

When the InP substrate 10 is etched, it is placed first on the substrate table 11. Then, trimethylamine ($(\text{CH}_3)_3\text{N}$) gas is introduced into the plasma generating chamber 1 through the gas introduction holes 7, and the RF-power is introduced into the plasma generating chamber 1 by inductive coupling from the coil 6 forming a plasma. Positive ion species from the plasma are accelerated towards the InP substrate 10 by the voltage obtained between the extraction grid 3 and the acceleration grid 4 by the applied grid biases. The ion energy of the ions impinging on the InP substrate 10 is determined by the bias applied to the acceleration grid 4 due to grounding of the substrate table 11. The impinging ions etch the InP substrate 10.

A parallel plate type etching apparatus such as shown in Figure 2, rather than the ion beam etching apparatus, may also be used. In this parallel type etching apparatus, RF electric power having frequency of 13.56 MHz is supplied between the opposed electrodes, thereby forming the etching

gas in an etching chamber into plasma so as to etch a substrate 1. The chamber has gas inlets 2 and a gas exhaust 3.

5 In a diode type etching apparatus as shown in Figure 9, RF electric power having a frequency of 13.56 MHz is supplied to the electrode, on which a substrate 1 is situated, thereby forming the etching gas in an etching chamber into plasma so as to etch a substrate. The walls of the chamber are grounded. The chamber has gas inlets 2
10 and a gas exhaust 3.

In the ECR etching apparatus of Figure 3, the chamber has a gas inlet 2 and a gas exhaust 3 and a mounting for a substrate 1. Microwave input is provided at 4 and magnets 5 are used to enhance the power coupling.

15 In the (ICP) type etching apparatus of Figure 4, again the chamber supports a substrate 1 and has a gas inlet 2 and a gas exhaust 3.

The barrel reactor etching apparatus of Figure 5 has a gas inlet 2 and a gas exhaust 3 and supports the substrate
20 1 as shown.

Further, an ion beam etching apparatus having any type of plasma source, and in particular an ECR plasma source such as shown in Figure 6 or an ICP source such as shown in Figure 1, may also be used. In Figure 6 the substrate is
25 carried at 1 and the chamber has a gas inlet 2 and a gas exhaust 3. Voltage grids are provided, together with a magnet 5 used to enhance the power coupling and a microwave

input 6.

Although the following detailed description refers to the use of an Ion Beam Etching apparatus, other types of high and low density plasma tools which are well known to those skilled in the art (including those outlined above) can also be used.

(2) Description of a method for etching an InP substrate according to an embodiment of the present invention.

First, a resist is coated onto the InP substrate by a spin coating method. Then the coated resist is hardened by baking so as to form a resist film having a thickness 1.2 μ m. Then, the resist film is exposed selectively using a photo mask, and thereafter unnecessary portions are removed by soaking the substrate into a developer, thus completing a resist mask 12 having openings as shown in Figure 7A. In Figure 7A the substrate 1 is shown with a completed resist mask 12.

Next, using the inductively coupled plasma ion beam etching apparatus as shown in Figure 1, the InP substrate 10 with the resist mask is placed on the substrate table 11 in the etching chamber 2. Then, the interior of the etching chamber 2 and the interior of the plasma generating chamber 1 are exhausted.

After a predetermined base pressure is reached, trimethylamine gas is introduced into the plasma generating chamber 1 and the pressure is held at 1.0×10^{-4} Torr to

6.0x10⁻⁴ Torr by varying the gas flow due to constant pumping speed. In case of the present embodiment, the pressure is held at 2.0x10⁻⁴ Torr and the trimethylamine gas flow is held, for instance, at 3 sccm. Furthermore, RF-power of 170 W is introduced to the plasma generating chamber 1. With this, the trimethylamine is formed into a plasma through inductively coupling of the RF-power. The plasma gas passes through the acceleration grid 4 and the extraction grid 3 into the etching chamber 2 and the ionised species are accelerated towards the InP substrate 10, impinging and thus starting etching. In other high density embodiments, the acceleration of the ionised species is achieved by means of applying an electrical bias, means of application being well known to those skilled in the art. This acceleration bias plays a critical role during the etching process. After etching, the resist mask is removed by acetone as shown on Figure 7B. Any remaining resist residuals are removed by oxygen plasma treatment.

(3) Next the results of the above etching will be described.

Figure 8 shows a scanning electron microscopy picture of an etched test structure in InP after etching for 30 min having a trimethylamine flow of 3 sccm and a pressure at 2.0x10⁻⁴ Torr. The biases on the extraction grid 3 and the acceleration grid 4 were kept at -300 V and +300 V respectively with respect to the grounded substrate table

11.

Table 1 shows the rms. roughness of etched InP surfaces measured by atomic force microscopy. The etch depths are in all cases 200 nm.

5 Column 1 in table 1 shows the rms. roughness of InP surfaces etched using trimethylamine (TMA) gas as described above for different energies of the impinging ions. Only the acceleration grid voltage and the process time were varied while all other parameters were kept constant.

10 Column 2 in table 1 shows a diagram of the rms. roughness of InP surfaces etched as described above, but with a mixture of trimethylamine (TMA) and Ar gas at different energies of the impinging ions. Only the acceleration grid voltage and process time were varied
15 while all other parameters were kept constant. The etching was performed under similar conditions as those demonstrated in column 1 in table 1 and in the same etching apparatus. Gas flows of trimethylamine and Ar were 3 sccm and 5 sccm respectively.

20 Column 3 in table 1 shows a diagram of the rms. roughness of InP surfaces etched using standard Ar sputtering with different ion energies of the impinging ions. Only the acceleration grid voltage and process time were varied while all other parameters were kept constant.
25 The etching was performed under similar conditions as those demonstrated in column 1 in table 1 and in the same etching apparatus. Ar gas flow was 5 sccm.

From the result of the atomic force microscopy observation, it is seen that the trimethylamine based process can produce extremely smooth morphologies (i.e. low rms. roughness) compared to standard Ar milling. Thus by
5 using an etching method of an embodiment of the present invention, it is possible to obtain extremely smooth etched InP surface morphologies.

Claims

1. A method of etching a substrate provided with pre-defined masked regions, whose elemental constituents are selected from Groups III and V or from groups II and VI of the Periodic Table, comprising the steps of: a) forming a gas containing molecules having at least one methyl group (CH_3) linked to nitrogen into a plasma; and b) etching the unmasked regions of the substrate by means of the plasma.

2. The method according to Claim 1, wherein said etching gas is selected from the group consisting of methylamine (CH_3NH_2), dimethylamine ($(\text{CH}_3)_2\text{NH}$) and trimethylamine ($(\text{CH}_3)_3\text{N}$).

3. A method of etching a substrate provided with pre-defined masked regions, whose elemental constituents are selected from Groups II and VI of the Periodic Table, comprising the steps of: a) forming an etching gas comprising trimethylamine ($(\text{CH}_3)_3\text{N}$) into a plasma; and b) etching the unmasked regions of the substrate by means of the plasma.

4. The method according to any one of Claims 1 and 3, wherein said etching gas is mixed with another gas selected from H_2 , N_2 , O_2 , Ar or another rare gas, or Cl_2 , BCl_3 or other halogen-containing gas or any combination of these.

5. A method according to any one of Claims 1 to 4, wherein said step (a) comprises forming the gas into a plasma by supplying microwave electric power with a

magnetic field to the etching gas.

6. A method according to any one of Claims 1 to 4, wherein said step (a) comprises forming the gas into a plasma by supplying microwave electric power to the etching gas.

7. A method according to any one of Claims 1 to 4, wherein said step (a) comprises forming the gas into a plasma by supplying radio frequency electric power to the etching gas.

8. A method according to any one of Claims 1 to 4, wherein said step (a) comprises forming the gas into a plasma by supplying DC electric power to the etching gas.

9. A method according to any one of Claims 1 to 8, wherein the ions are accelerated by a DC bias.

10. A method according to Claim 9, wherein said DC bias creates energy in the range of 0-2000 eV.

11. A method according to any one of Claims 1 to 8, wherein the applied power is converted to an ion energy in the range of 0-2000 eV.

12. Any combination of novel features of a method of etching a substrate provided with pre-defined masked regions, substantially as herein described and/or as illustrated in the accompanying drawings.

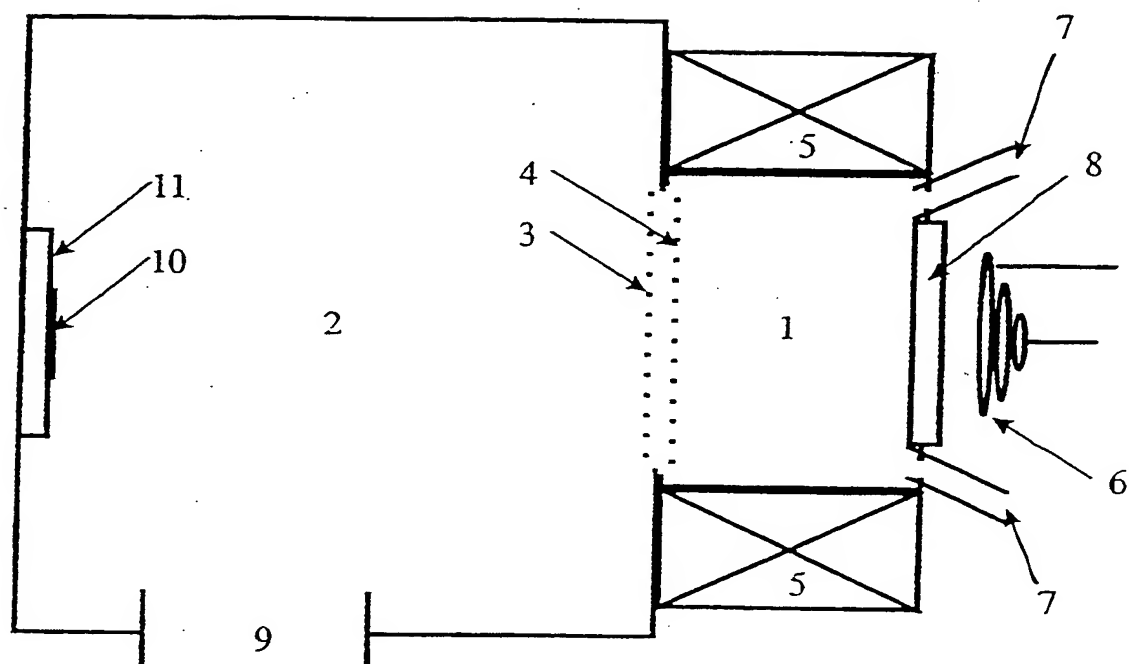


Fig. 1

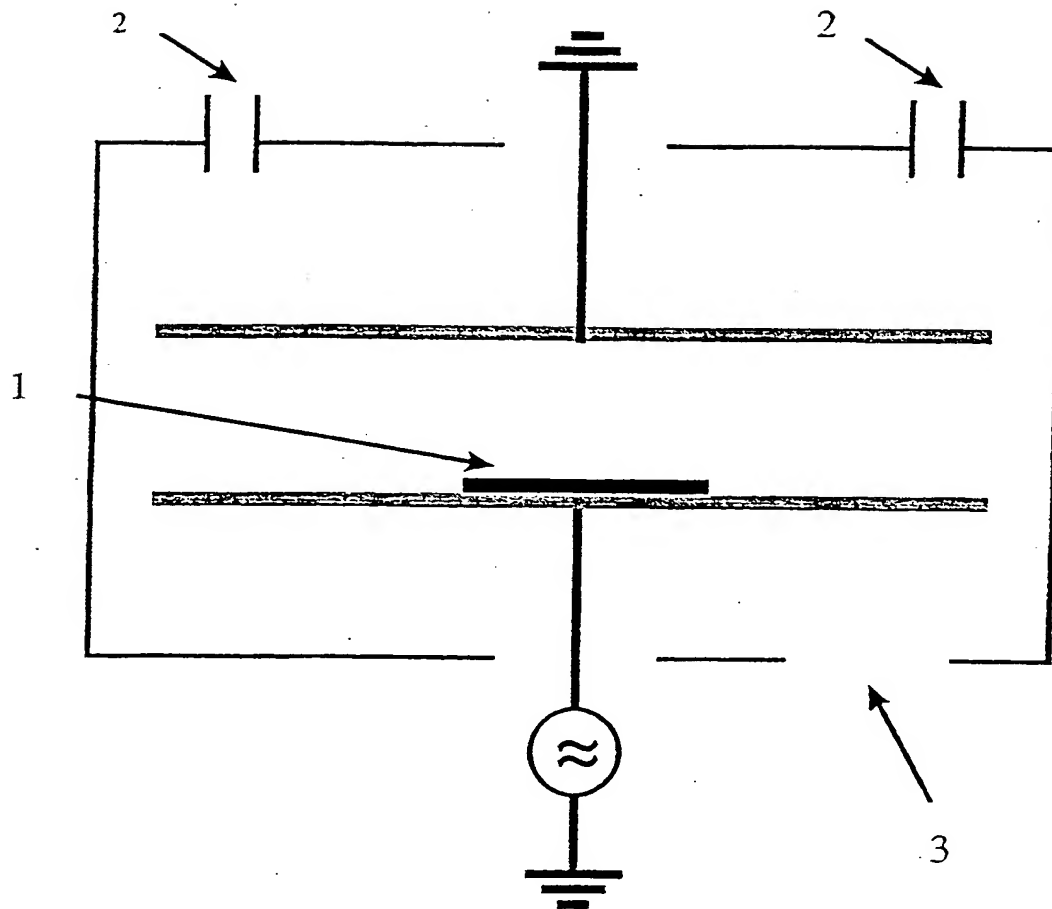


Fig. 2

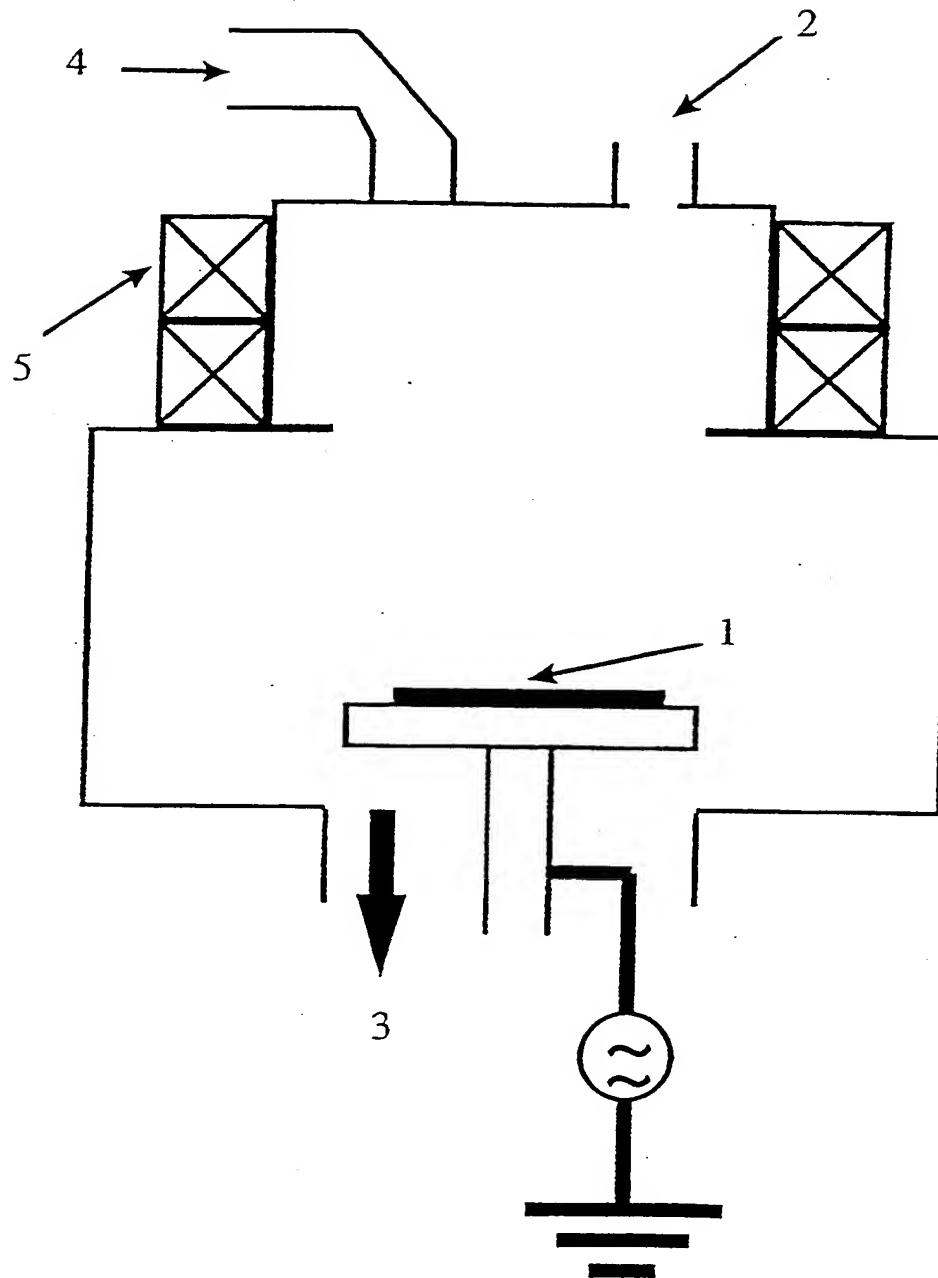


Fig. 3

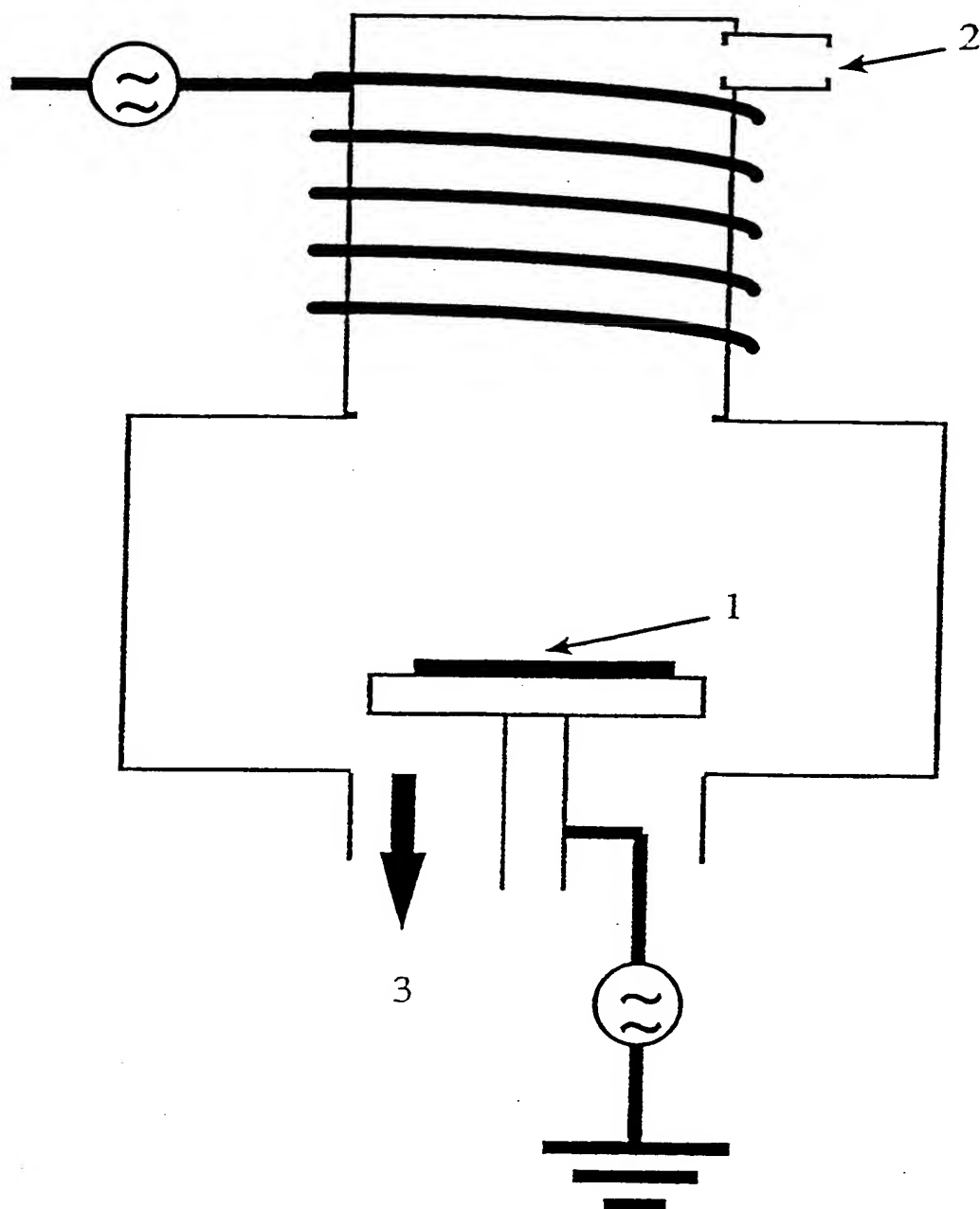


Fig. 4

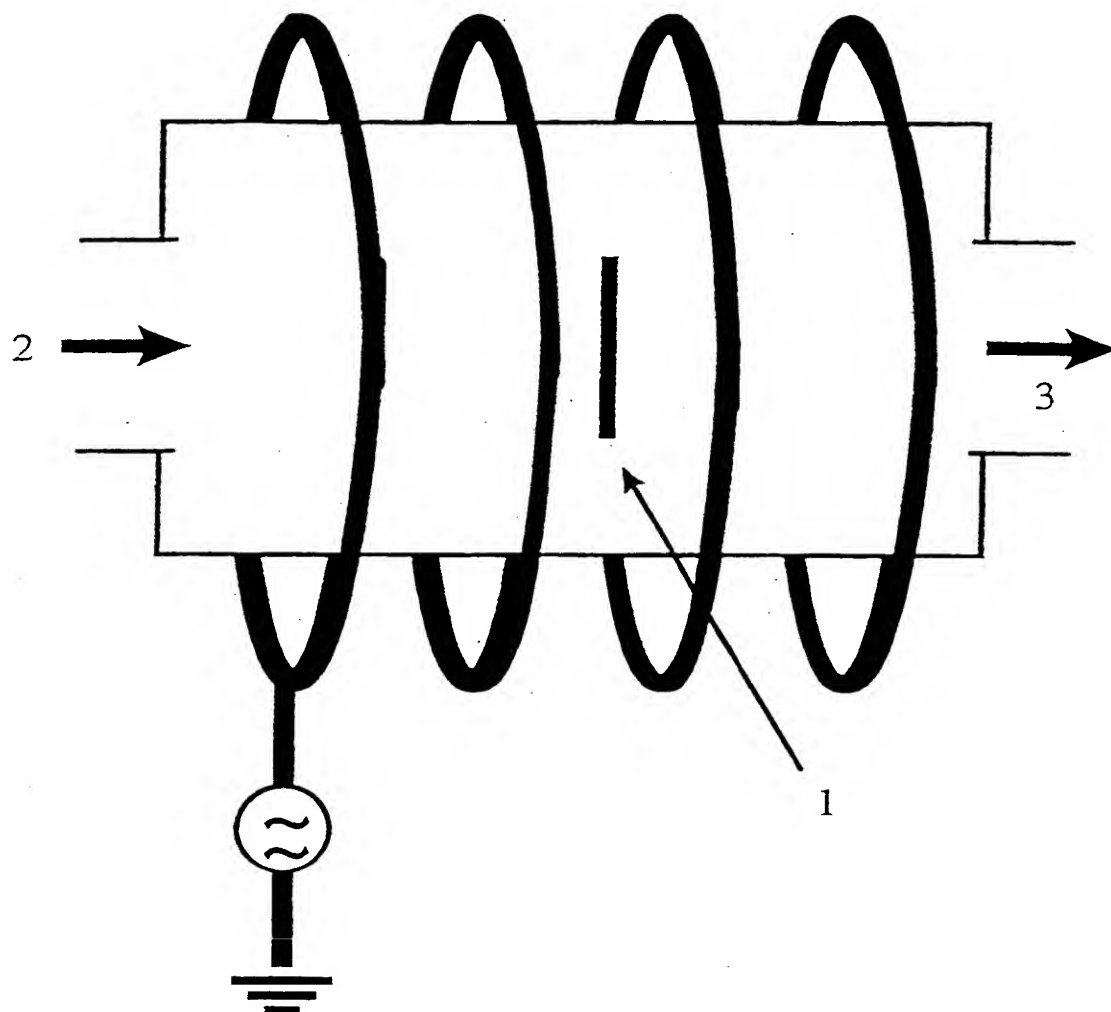


Fig. 5

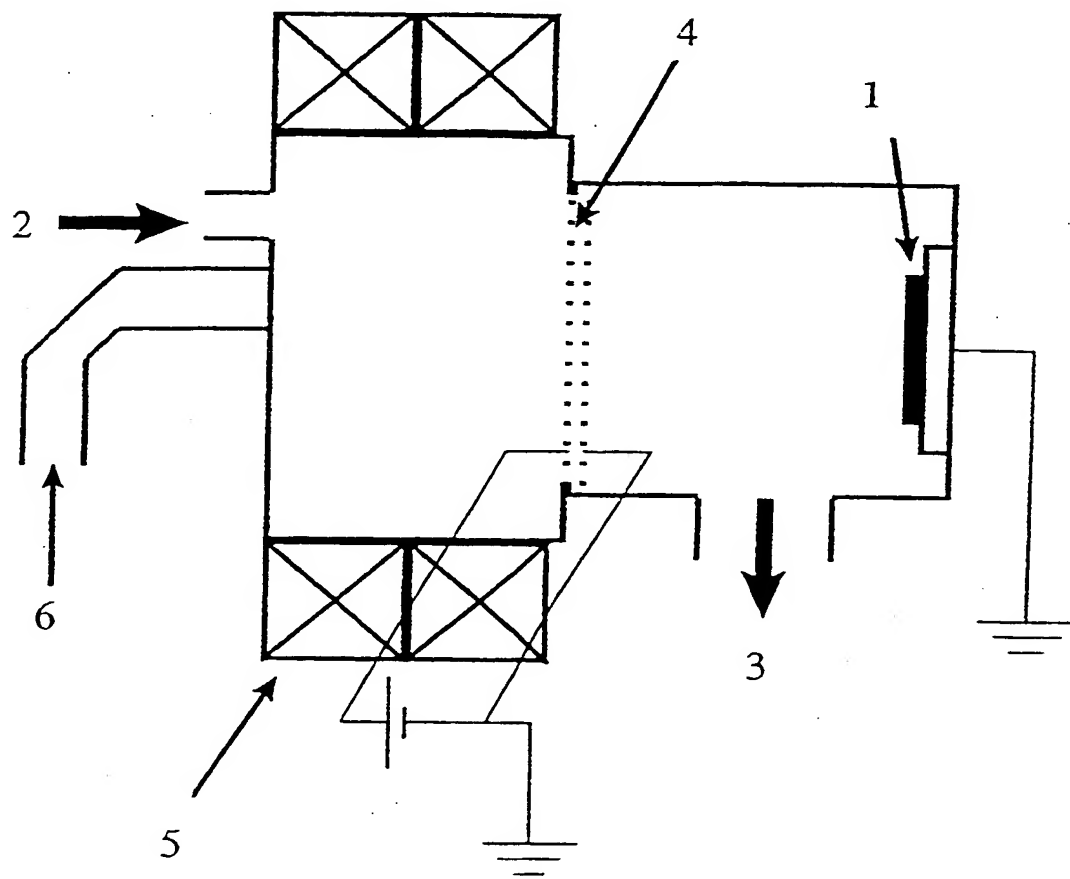
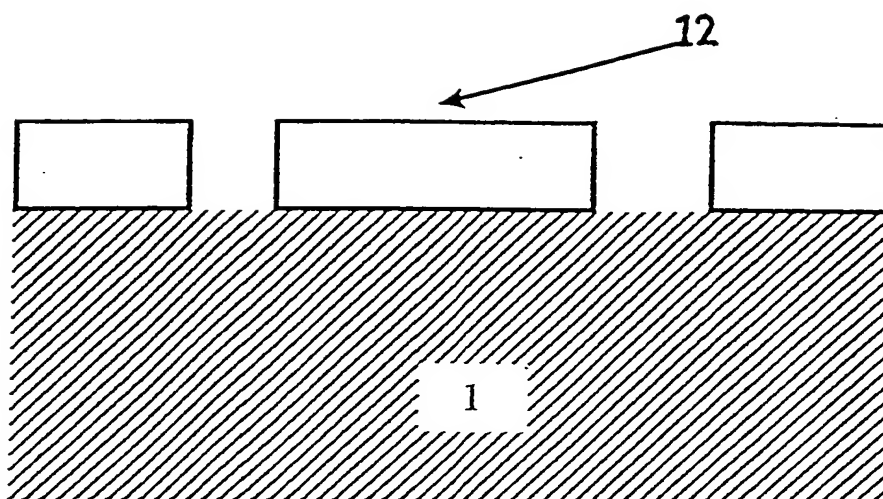


Fig. 6

A;



B;

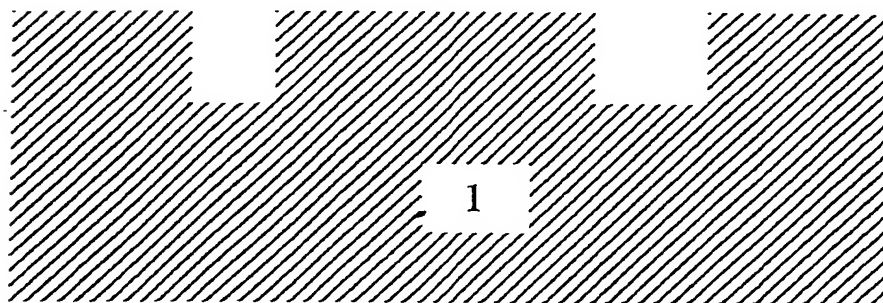


Fig. 7A-B

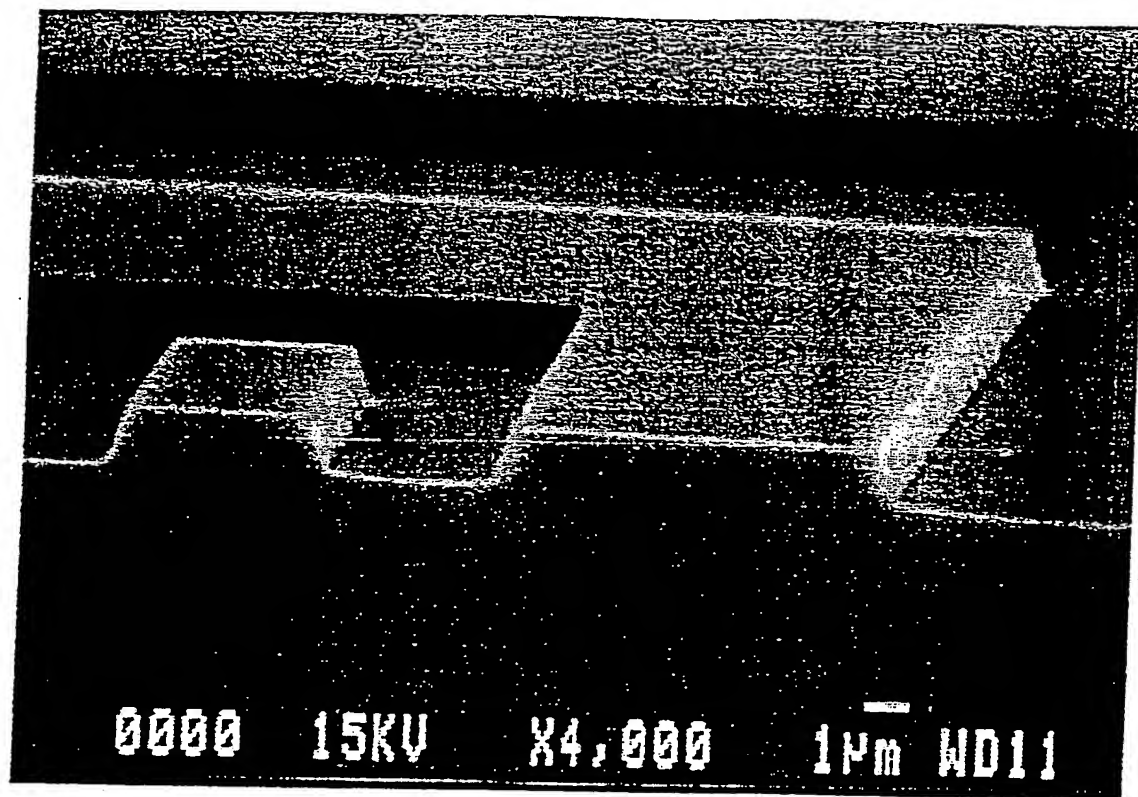


Fig. 8

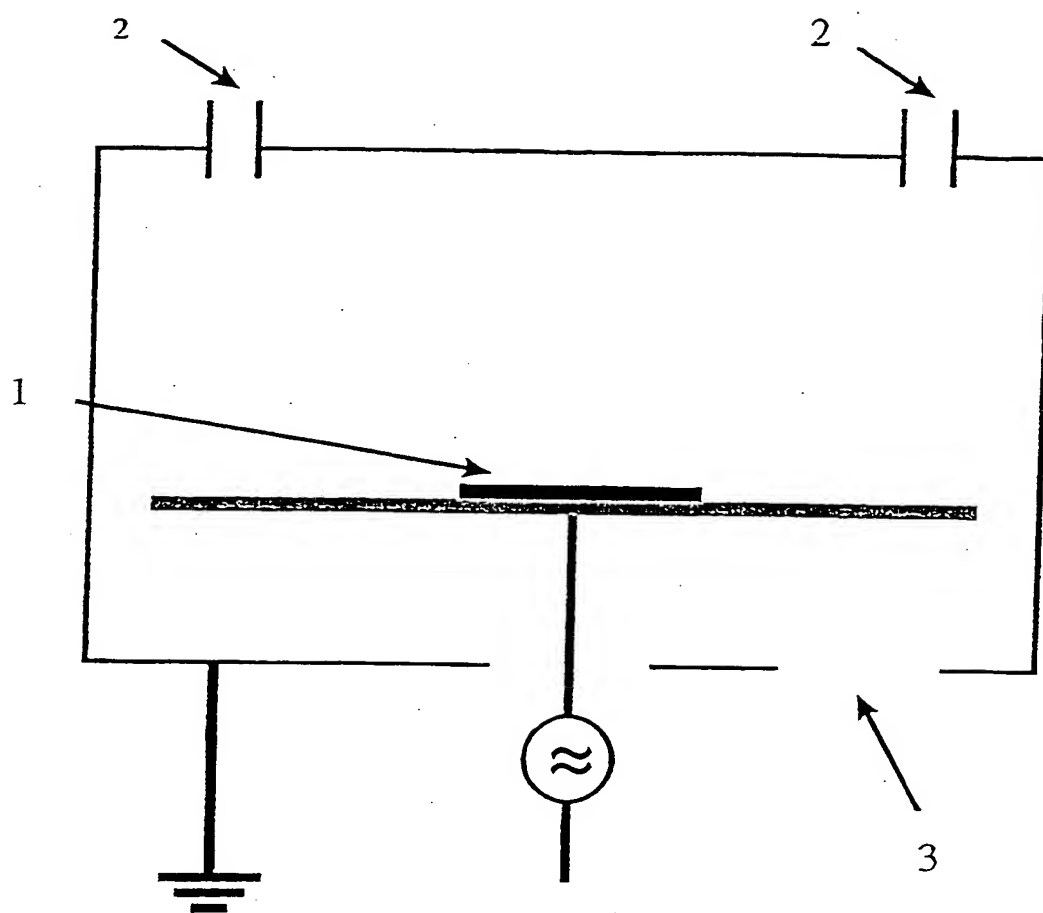


Fig. 9

		PROCESS GAS		
I O N E N E R G Y		TMA	TMA + Ar	Ar
	75 eV	0.65 nm	0.15 nm	4.80 nm
	150 eV	0.16 nm	0.19 nm	3.90 nm
	300 eV	0.26 nm	0.24 nm	13.70 nm
	500 eV	0.39 nm	1.1 nm	7.30 nm

Table 1

PCT

REC'D 02 OCT 2001

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference MJ/CS/STS.38	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/02255	International filing date (day/month/year) 21/06/2000	Priority date (day/month/year) 21/06/1999
International Patent Classification (IPC) or national classification and IPC H01L21/306		
Applicant SURFACE TECHNOLOGY SYSTEMS LIMITED		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 15/01/2001	Date of completion of this report 24.09.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Bernabé Prieto, A Telephone No. +49 89 2399 2224 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/02255

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-12 as originally filed

Claims, No.:

1-12 as originally filed

Drawings, sheets:

1/10-10/10 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
 - ☐ the language of publication of the international application (under Rule 48.3(b)).
 - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
 - ☐ filed together with the international application in computer readable form.
 - ☐ furnished subsequently to this Authority in written form.
 - ☐ furnished subsequently to this Authority in computer readable form.
 - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
 - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:
- ☐ the description, pages:
 - ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/02255

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims
	No: Claims 1-12
Inventive step (IS)	Yes: Claims
	No: Claims 1-12
Industrial applicability (IA)	Yes: Claims 1-12
	No: Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/02255

The comments relate to items I to VIII of the cover sheet, where the corresponding cases have been crossed.

1 Reference is made to the following documents:

D1: US-A-5 534 109 (FUJIWARA KOJI ET AL) 9 July 1996 (1996-07-09)

D2: PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 016896 A (FUJITSU LTD), 22 January 1999 (1999-01-22)

2 Claims 1-4 of the present application do not meet the requirements of Article 6 PCT.

2.1 The formulation in claim 1 " ... a gas containing molecules having at least one methyl group linked to nitrogen" is unduly broad. This broad formulation includes gases which are susceptible of polymerising, which is clearly undesired in the etching process of the present application (cf. e. g. page 2, lines 9-12). Thus, claim 1 is not supported by the description.
It appears also that not any halogen containing gas (cf. claim 4) may be suitable for the etching process.

2.2 Claims 2 and 3 disclose the same subject-matter, thus resulting in a lack of conciseness of the claims.

3 The present application does not comply with Article 33(2) PCT because the subject-matter of claims 1-12 is not new in view of the disclosure of document D1 (cf. claim 3; column 3, lines 12-56; column 6, lines 45-56).

4 The present application does not comply with Article 33(2) PCT because the subject-matter of claim 1 is not new in view of the disclosure of document D2 (cf. Abstract) in particular, in respect of the etching of III-V- semiconductor compounds.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/02255

- 5 Notwithstanding items 3 and 4, above, the present application does not comply with Article 33(3) PCT because the subject-matter of claims 1-12 does not involve an inventive step.
- 5.1 Concerning claims 1-3, the skilled person knowing from D1 (cf. claim 3) that the method is successfully used for a II-VI semiconductor HgCdTe substrate, would immediately try to apply it to, at least, other semiconductor compounds of the same family (i. e. other II-VI semiconductor compounds).
- 5.2 Concerning claim 4, the use of fluorides and/or inert gases (as etchants or carriers) are already per se well-known in semiconductor etching processes.
- 5.3 Concerning claims 5-11, the suitable accelerating (and non-damaging; cf. D1) voltage in a RIBE process is obtained by the skilled person as a matter of common experimental procedure.
- 6 The following deficiencies should also be noted:
- 6.1 Claim 12 contains a reference to the description and the drawings. Such a reference is only allowable when absolutely necessary (Rule 6.2 (a) PCT), which is not the present case.
- 6.2 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D2 is not mentioned in the description, nor are these documents identified therein.
- 6.3 Independent claim 1 is not in the two-part form in accordance with Rule 6.3(b) PCT, which in the present case would be appropriate, with those features known in combination from the prior art being placed in a preamble (Rule 6.3(b)(i) PCT) and with the remaining features being included in a characterising part (Rule 6.3(b)(ii) PCT).
- 6.4 The features of the claims are not provided with reference signs placed in parentheses (Rule 6.2(b) PCT).

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

JAMES, M.J.G.
Wynne-Jones, Lainé & James
22 Rodney Road
Cheltenham
Gloucestershire GL50 1JJ
GRANDE BRETAGNE

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of mailing
(day/month/year) 30.03.2001

Applicant's or agent's file reference
MJ/CS/STS.38

REPLY DUE within 2 month(s) and 15 days
from the above date of mailing d. 27-4-01

International application No.
PCT/GB00/02255

International filing date (day/month/year)
21/06/2000

Priority date (day/month/year)
21/06/1999

International Patent Classification (IPC) or both national classification and IPC
H01L21/306

Applicant

SURFACE TECHNOLOGY SYSTEMS LIMITED

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.
2. This opinion contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain document cited
 - VII ☒ Certain defects in the international application
 - VIII ☒ Certain observations on the international application
3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 21/10/2001.

Name and mailing address of the international preliminary examining authority:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner

Bernabé Prieto, A

Formalities officer (incl. extension of time limits)

Reddy, J
Telephone No. +49 89 2399 2231



I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*);

Description, pages:

1-12 as originally filed

Claims, No.:

1-12 as originally filed

Drawings, sheets:

1/10-10/10 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-12 (NO)
Inventive step (IS)	Claims	1-12 (NO)
Industrial applicability (IA)	Claims	1-12 (YES)

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

The comments relate to items I to VIII of the cover sheet, where the corresponding cases have been crossed.

1 Reference is made to the following documents:

D1: US-A-5 534 109 (FUJIWARA KOJI ET AL) 9 July 1996 (1996-07-09)

D2: PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 016896 A (FUJITSU LTD), 22 January 1999 (1999-01-22)

2 Claims 1-4 of the present application do not meet the requirements of Article 6 PCT.

2.1 The formulation in claim 1 " ... a gas containing molecules having at least one methyl group linked to nitrogen" is unduly broad. This broad formulation includes gases which are susceptible of polymerising, which is clearly undesired in the etching process of the present application (cf. e. g. page 2, lines 9-12). Thus, claim 1 is not supported by the description.

It appears also that not any halogen containing gas (cf. claim 4) may be suitable for the etching process.

2.2 Claims 2 and 3 disclose the same subject-matter, thus resulting in a lack of conciseness of the claims.

3 The present application does not comply with Article 33(2) PCT because the subject-matter of claims 1-12 is not new in view of the disclosure of document D1 (cf. claim 3; column 3, lines 12-56; column 6, lines 45-56).

4 The present application does not comply with Article 33(2) PCT because the subject-matter of claim 1 is not new in view of the disclosure of document D2 (cf. Abstract) in particular, in respect of the etching of III-V- semiconductor compounds.

- 5 Notwithstanding items 3 and 4, above, the present application does not comply with Article 33(3) PCT because the subject-matter of claims 1-12 does not involve an inventive step.
- 5.1 Concerning claims 1-3, the skilled person knowing from D1 (cf. claim 3) that the method is successfully used for a II-VI semiconductor HgCdTe substrate, would immediately try to apply it to, at least, other semiconductor compounds of the same family (i. e. other II-VI semiconductor compounds).
- 5.2 Concerning claim 4, the use of fluorides and/or inert gases (as etchants or carriers) are already per se well-known in semiconductor etching processes.
- 5.3 Concerning claims 5-11, the suitable accelerating (and non-damaging; cf. D1) voltage in a RIBE process is obtained by the skilled person as a matter of common experimental procedure.
- 6 The following deficiencies should also be noted:
- 6.1 Claim 12 contains a reference to the description and the drawings. Such a reference is only allowable when absolutely necessary (Rule 6.2 (a) PCT), which is not the present case.
- 6.2 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D2 is not mentioned in the description, nor are these documents identified therein.
- 6.3 Independent claim 1 is not in the two-part form in accordance with Rule 6.3(b) PCT, which in the present case would be appropriate, with those features known in combination from the prior art being placed in a preamble (Rule 6.3(b)(i) PCT) and with the remaining features being included in a characterising part (Rule 6.3(b)(ii) PCT).
- 6.4 The features of the claims are not provided with reference signs placed in

parentheses (Rule 6.2(b) PCT).

- 7 In order to facilitate the examination of the conformity of the amended application with the requirements of Article 34(2)(b) PCT, the applicant is requested to clearly identify the amendments carried out, no matter whether they concern amendments by addition, replacement or deletion, and to indicate the passages of the application as filed on which these amendments are based (see also Rule 66.8(a) PCT). If the applicant regards it as appropriate these indications could be submitted in handwritten form on a copy of the relevant parts of the application as filed.